

Claims

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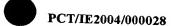
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- 1. A CO<sub>2</sub> sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.
- 2. A CO<sub>2</sub> sensor as claimed in claim 1 wherein the pH indicator is selected from the group consisting of pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.
- A CO<sub>2</sub> sensor as claimed in claim 1 or 2 wherein the long-lived reference luminophore is selected from the group consisting of a luminescent complex, in particular [Ru<sup>II</sup>-tris(4,7-diphenyl-1,10-phenanthroline)]Cl<sub>2</sub>, ruthenium-based compounds with α-diimine ligands, luminescent transition metal complexes with platinum metals Ru, Os, Pt, Ir, Re or Rh as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate,
  ruby, alexandrite and Nd-Yag.
  - 4. A CO<sub>2</sub> sensor as claimed in any preceding claim wherein the porous sol-gel matrix is selected from the group consisting of a methyltriethoxysilane (MTEOS) solgel matrix, hybrid (organic-inorganic) sol-gel matrices including ethyltriethoxysilane (ETEOS), phenyltriethoxysilane (PhTEOS), n-octyl TEOS and methyltrimethoxysilane (MTMS), and UV-curable sol-gels, soluble ormosils, or hybrid polymer matrices.
- 5. A CO<sub>2</sub> sensor as claimed in any preceding claim wherein the luminophore is a ruthenium-doped sol-gel particle, in particular [Ru<sup>II</sup>-tris(4,7-diphenyl-1,10-phenanthroline)]Cl<sub>2</sub>. -doped particles.

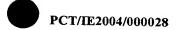
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- 6. A CO<sub>2</sub> sensor as claimed in any preceding claim wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a sol-gel matrix.
- 7. A combined O<sub>2</sub>/CO<sub>2</sub> sensor comprising:-
- 5 (a) an O<sub>2</sub> sensor comprising an oxygen sensitive luminescent complex immobilised in a porous sol-gel matrix, and
  - (b) an CO<sub>2</sub> sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.
  - 8. A combined O<sub>2</sub>/CO<sub>2</sub> sensor wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a porous sol-gel matrix.
  - 9. A combined O<sub>2</sub> / CO<sub>2</sub> sensor as claimed in claim 8 wherein the ruthenium-complex is selected from the group consisting of an oxygen sensitive luminescent complex such as ruthenium-based compounds with α-diimine ligands and luminescent transition metal complexes with platinum metals (Ru, Os, Pt, Ir, Re or Rh) as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.
- 10. A combined O<sub>2</sub> / CO<sub>2</sub> sensor as claimed in claim 8 or claim 9 wherein the
  25 immobilised O<sub>2</sub> sensor and the immobilised CO<sub>2</sub> sensor are coated onto the same substrate.
  - 11. A combined  $O_2$  /  $CO_2$  sensor as claimed in claim 8 to 10 wherein the two sensors are coated onto the substrate side-by-side.
  - 12. A combined O<sub>2</sub> / CO<sub>2</sub> sensor as claimed in any of claims 5 to 8 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate



materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

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- 13. A method of making a CO<sub>2</sub> sensor comprising:
- (1) synthesis of an Ru(dpp)<sub>3</sub>(TSPS)<sub>2</sub> ion-pair comprising mixing dissolved Ru(dpp)<sub>3</sub>Cl<sub>2</sub> with trimethylsilylpropane sulfonic acid, sodium salt and allowing the ion-pair to precipitate,
- (2) synthesis of the particles comprising condensing the dissolved Ru(dpp)<sub>3</sub>(TSPS)<sub>2</sub> ion-pair with TEOS and halting the condensation reaction with alcohol, washing the condensate with alcohol and drying the condensate, and
  - (3) and fabrication of the CO<sub>2</sub> sensor films comprising either (a.) suspending the doped reference particles in the coimmobilisation matrix solution, mixing the coimmobilisation matrix solution into a pH indicator solution which comprises a pH indicator in a quaternamentary of the desired product of the coimmobilisation matrix.
  - indicator in a quaternary ammonium hydroxide solution, and saturating the mixture immediately with CO<sub>2</sub> followed by deposition onto a substrate or (b.) a dual-layer configuration where a low oxygen-sensitivity ruthenium complex is sealed in an oxygen impermeable layer and over-coated with the HPTS-based CO<sub>2</sub> sensing layer.

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14. A method as claimed in claim 13 wherein the quaternary ammonium hydroxide is selected from the group consisting of cetyl-trimetyl ammonium hydroxide (CTA-OH), tetra-octyl ammonium hydroxide (TOA-OH) or tetra-butyl ammonium hydroxide (TBA-OH) or other quaternary ammonium hydroxides.

- 15. A method as claimed in claim 13 or 14 wherein the pH indicator is selected from the group consisting pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.
- 30 16. A packaging medium having a combined CO<sub>2</sub> sensor and an O<sub>2</sub> sensor as claimed in any of claims 8 to 12 formed on a surface of the medium which will lie internally of the package when the package is formed.

17. A packaging medium as claimed in claim 16 wherein the sensors are formed on the packaging medium by a method selected from the group consisting of dipcoating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

18. A quality control method comprising reading a combined  $O_2$  /  $CO_2$  sensor as claimed in any of claims 8 to 12, formed on the internal surface of a package, with an optical reader, and determining the levels of  $O_2$  and  $CO_2$  inside the package in relation to a control.

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- 19. A method of screen-printing a combined O<sub>2</sub> /CO<sub>2</sub> sensor as claimed in any of claims 8 to 12 onto a substrate comprising forcing the sensor sol through a mask or mesh and drying the substrate.
- 15 20. A method of ink-jet printing a combined O<sub>2</sub> /CO<sub>2</sub> sensor as claimed in any of claims 5 to 9 onto a substrate comprising filling an ink reservoir of an ink-jet printer with sensor sol and printing the sensor sol onto the substrate using an ink-jet printer.
- 21. A method of forming a gas-sensitive sensor on a substrate comprising coating or printing the substrate with a porous sol-gel matrix comprising a gas sensitive indicator.
  - 22. A method as claimed in claim 21 wherein the gas sensitive indicator is an oxygen-sensitive luminescent complex.

- 23. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and a long-lived reference luminophore.
- 24. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and the substrate is further provided with separate oxygen impermeable layer comprising a long-lived reference luminophore.
  - 25. A method as claimed in any of claims 21 to 23 wherein two gas sensors are formed on the substrate.

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- 26. A method as claimed in any of claims 21 to 25 wherein the sensor is formed on the substrate by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.
- 27. A method as claimed in any of claims 21 to 26 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.
- 15 28. A method as claimed in any of claims 21 to 27 wherein the sensor is a luminophore-based sensor.
  - 29. A method as claimed in any of claims 21 to 27 wherein the sensor is a colorimetric-based sensor.
  - 30. A substrate having a gas-sensitive sensor formed thereon wherein the sensor comprises a sol-gel matrix comprising a gas sensitive indicator and the sensor has been formed by printing or coating.
- 31. A substrate as claimed in claim 30 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic cap.